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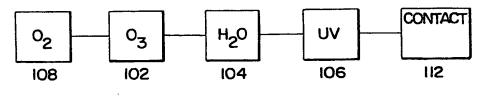
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(54) Title: STERILIZATION PROCESS FOR AIR, LIQUID AND SURFACES





(57) Abstract: A sterilization apparatus has an oxygen concentrator (108) which produces oxygen gas. The oxygen concentrator is connected to an ozone generator (102) whereby ozone is generated in the oxygen gas. The resulting gas is humidified to form a humidified ozone/oxygen mixture. The mixture is irradiated with ultraviolet light (106) to form a sterilant of hydrogen peroxide, ozone, hydroxyls, and oxygen ions. The sterilant is moved from a creation chamber to a contact chamber (112) whereby the sterilant is applied to living matter. The living matter is rendered nonviable. In a method of sterilization, a sterilant gas is formed by concentration oxygen, generating ozone from the oxygen, humidifying the mixture of ozone and oxygen, irradiating the humidified mixture of ozone and oxygen with ultraviolet light forming a sterilant that can be remotely delivered.

STERILIZATION PROCESS FOR AIR, LIQUID AND SURFACES

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

The present invention generally deals with methods and apparatuses for rendering living matter, particularly microorganisms non-viable. More specifically, the methods deal with creating a sterilizing agent of hydrogen peroxide (H_2O_2) and other oxidizing agents in sufficient concentrations to ensure almost 100% non-viability of microorganisms with appropriate exposure times. The apparatuses generate the required sterilizing agent from ozone (O_3), moisture and ultraviolet light. Systems use the sterilizing agent to treat water, air and material surfaces to prevent contamination and disease and to control waste.

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PRIOR ART

In this age of heightened awareness of health hazards it has become more difficult to kill or even control biological threats. In view of the greater regulation of the food we eat, the water we drink, the air we breathe and the property we own, the public has demanded better disinfection methods and machines. Recent news reports have made the public aware of the threats. The news media has widely covered many different cases wherein biological contaminants have caused hospitalization and even death. Almost daily there

are news reports of listeria outbreaks, new cases of Hepatitis A, B and C, widespread influenza outbreaks or even the now mundane pollution reports where an overabundance of E. coli bacteria have made a beach or recreation spot unusable.

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The U.S. military is concerned with dangerous chemical and biological weapons that are being used as the rules of combat have changed. Terrorists are no longer constrained by the same factors as those that limited weapon manufacturers during the cold war. Leading microbiologists, disaster planners, municipal emergency response leaders, experts in emerging disease, national security experts, politicians, military strategists and scientists, the FBI, the White House and even the United Nations have been gripped by a new found sense of urgency that chemical bioterrorism, formerly dismissed by most in the scientific and military arena as the unthinkable alternative, must now be taken seriously.

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In the field of municipal water treatment, much concern has been expressed recently regarding the safety of using chlorine for water purification. Studies have indicated that chlorination of water supplies can be linked to an increased risk for certain types of cancer.

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Recently, much attention has been given to the issue of aircraft cabin air quality. Legislation is currently pending before both the Senate and the House of Representatives, which will mandate improvements in aircraft air quality. The Association of Flight Attendants has recently claimed that flight attendants are experiencing greater health risks as a result of poor air quality. In addition, health care journals such as "Emerging Infectious Diseases" and "Natural Way

Magazine" have published articles discussing the potential health risks of poor cabin air quality.

In the past, individuals have tried to solve these problems by many different methods. Some have used mechanical devices like filter systems. Many others tried chemistry and other weapons to combat the biological threats.

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One of the oldest methods for removing contaminants from a fluid, whether air or water, is filters. Whether treating drinking water, waste water or air, filters, if properly used and maintained, can be an effective weapon against biological contaminants. However, filters are often ignored. Typically, there is no preventative maintenance of filters and often times filters are not replaced at regular intervals. This results in ineffective biological contaminant removal. Often, the filters become breeding grounds for biological contaminants thus increasing their concentrations.

Air filters have often been used to treat microorganisms in the air. In HVAC systems in buildings, vehicles, or aircraft, owners often choose air filters. Air filters are expensive and must be regularly changed and the HVAC systems must be maintained. For a number of reasons, including cost, irregular maintenance and improper maintenance, filters fail and bacteria, viruses and microorganisms are not removed from the air. Even if the filters catch most of the living matter, the filters do not destroy the living matter, they only concentrate it. Even sophisticated filters, including reverse osmosis and HEPA filters, perform well, but the biological agents are never destroyed, only concentrated. The high concentration of biological agents may cause the filters

to break down. When the filter fails, high concentrations of both innocuous organisms and highly dangerous organisms can be released into the systems simultaneously. These organisms can produce serious illness and even death.

In order to filter out biological threats, a very fine filter must be used. This causes a huge pressure drop across the filter. In order to get the filter to perform properly, a relatively large fan or pump must be used to move fluids across the filter. These pumps are very expensive to purchase and operate.

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Another method for treating biological contaminants is with ozone. Ozone has been used for purification and sterilization since at least the early 1890's, when it was used to treat drinking water in Europe. Ozone is an unstable molecule comprised of three atoms of oxygen. It is formed by the excitation of molecular oxygen into atomic oxygen in an emerging environment. This allows the recombination of an excited oxygen atom with an excited oxygen molecule. Ozone is an unstable molecule. It is also a powerful oxidizing agent. Ozone in high enough concentrations is effective against both microbial contaminants and some volatile organic compounds and, because of its short half-life, ozone creates relatively low environmental impact in comparison to other sterilization methods. However, because ozone has a relatively short half-life, it breaks down into regular oxygen molecules rapidly, and, as a result, it generally must be generated on-site for sterilization processes.

Another known sterilant is Ultraviolet Light ("UV"). Ultraviolet light has been used on a commercial basis as an effective sterilant since about the beginning of the 20th century. Ultraviolet light, which is a form of electromagnetic radiation, is most effective as a sterilant when it is produced

in a frequency range of 220-300 nanometers (frequently referred to as the "abiotic" region), and is most effective when the germicidal wavelengths correspond with the wavelengths most absorbed by nucleic acids and when the materials to be sterilized are directly exposed to the radiation. Ultraviolet light radiation acts on cellular deoxyribonucleic acid (DNA) to effect lethal changes in microbes, and can be used in place of chlorine in water treatment without any adverse affects on wildlife and other organisms. Ultraviolet irradiation does not require the use of harmful chemicals and does not leave harmful residues, but it is not generally accepted in the United States, in part because it requires that the materials to be sterilized be directly exposed to the radiation.

Ultraviolet light alone is not particularly effective in killing microorganisms but is toxic in high concentrations, particularly in media with limited transmittance (murky water) or with complex surfaces that create shadowing. By combining ultraviolet light and low concentrations of ozone, a highly effective sterilant has been developed that is superior to either sterilant alone. The synergistic effect can be explained by the absorption of ultraviolet light by ozone to produce highly reactive substances that can effectively kill all microorganisms, including hard-to-kill spores.

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The combination of two well known sterilants, ultraviolet light and ozone, results in a more effective and relatively low cost and sterilization method. Singularly, neither ultraviolet light nor ozone are sufficiently effective in killing all types of microorganisms. When used in combination, however, a synergistic effect results in an enhanced effective rate of decontamination.

When ozone is exposed to ultraviolet light, singlet and triplet excited states of molecular oxygen and excited states of atomic oxygen are created.

In addition to the method used to effect sterilization, the sterilization processes used hereto before have varied greatly depending on the medium in which the biological matter is found. In order to treat water, currently aeration and chlorine are used, killing only some of the organisms. Neither method can destroy all the organisms or even nearly all the organisms. To get to high kill levels, the cost is tremendous.

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Additionally, the use of chlorine is getting more heavily regulated. The Food & Drug Administration ("FDA") has decided that Americans should not ingest chlorine in large quantities. As such, treatment and removal of the residue is getting more expensive. Meanwhile, organisms are developing a resistance to chlorine which requires the use of more chlorine to be as effective.

Another problem with chlorine is the requirement for high residual time. Chlorine treatment is designed to be the final treatment stage in potable water treatment. Water treatment processes are designed to put enough chlorine in the water so that the chlorine in the water does not dissipate until the water is used. However, since the chlorine treatment is done at a central facility, those close to the central treatment facility taste and smell the chlorine residue. This residue is rather unpleasant. However, those far away from the central treatment facility receive water which was not treated with enough chlorine to kill all the bacteria. Similarly, when treating surfaces with chlorine, the same problems are present — either too much chlorine leaving residue or too little chlorine, leaving bacteria still living.

In an attempt to devise a better sterilization process for food stuffs, a gamma radiation sterilization process was developed. The gamma radiation renders virtually all living organisms non-viable, however special precautionary measures are needed to protect operators and consumers of sterilized products. Additionally, any process using gamma radiation is highly regulated by the FDA. Currently, any substance subjected to gamma radiation must bear a warning "IRRADIATED". Even though "IRRADIATED" food is generally considered safe, public opinion has kept "IRRADIATED" food out of stores.

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SUMMARY OF THE INVENTION

The present invention recognizes and addresses the foregoing disadvantages, and other prior art methods and apparatuses.

Accordingly, an object of the present invention is to sterilize air, liquids and surfaces with a sterilizing agent.

Another object of the present invention is to sterilize more thoroughly in shorter periods of time.

Still another object of the present invention is to develop an agricultural product storage device.

And yet another object of the present invention is to develop a run-off and low flow water treatment system.

Still yet another object of the present invention is to develop a heating, ventilation and air conditioning (HVAC) treatment system.

Another object of the present invention is to provide a more efficient sterilization device capable of minimal maintenance effort.

Yet another object of the present invention is to provide a lower cost sterilization method, systems and devices.

And yet another object of the present invention is to provide a sterilizing agent generator that can produce varying concentrations of sterilizing agent for sterilization methods.

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These and other objects of the present invention are achieved by providing a sterilizing agent generator having (a) an oxygen concentrator that creates a supply of O_2 from the air, (b) an O_3 generator, that makes O_3 from the supply of O_2 , (c) a moisture control device that regulates the humidity or moisture in the supply of O_2/O_3 mixture, and (d) a UV light that generates UV in the presence of O_3 and moisture to produce a sterilizing agent. In another embodiment, at least one sensor is present that can measure the presence of at least one of H_2O_2 , moisture, O_3 , and UV.

In another embodiment of the invention, the sterilizing agent generator is connected to a mixing chamber wherein the sterilizing agent is brought into contact with living matter whereby the living matter is made non-viable.

In yet another embodiment of the invention, the sterilizing agent generator, generates sterilizing agent until an appropriate concentration is reached, then a mixing device moves the sterilizing agent into a mixing chamber whereby the sterilizing agent is mixed so that the living matter in the mixing chamber is brought into contact with the sterilizing agent. The living matter is thereby made non-viable.

In another embodiment of the invention, a sterilizing agent is remotely created from oxygen, ozone, moisture, and ultraviolet light. The resulting

sterilizing agent has at least H_2O_2 , singlet oxygen, oxygen ions, ozone and hydroxyls. The sterilizing agent is delivered to a contact area whereupon, the sterilizing agent contacts living matter and renders it non-viable. The living matter can be on a surface, in the air, in water, or mixed in a permeable medium that the sterilizing agent can penetrate.

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Still another embodiment of the invention, a sterilizing agent is created whereby the effectiveness of the sterilizing agent is controlled by altering the concentration of ozone and oxygen and the concentrations of hydrogen peroxide and other oxidizing agents by controlling the moisture content and exposure intensity and time to ultraviolet light

Another embodiment of the invention is an agricultural product storage device. The agricultural product storage device has at least one sterilizing agent source that releases the sterilizing agent into the air making a gaseous sterilizing agent. The gaseous sterilizing agent is circulated around the agricultural products contacting microorganisms and other living matter, rendering them non-viable. In a preferred embodiment, the sterilizing agent source is a sterilizing agent generator as described herein.

In yet another embodiment of the invention, liquids are mixed with a gaseous sterilizing agent. In one embodiment, the sterilizing agent is bubbled through the liquid until a desired level of living matter is made non-viable.

In another embodiment of the invention a run-off or low flow water treatment system creates a sterilizing agent remotely. The sterilizing agent is then brought into contact with the water in a treatment chamber to make living matter in the water non-viable. Preferably, the run-off water or low flow water

is recycled through the treatment chamber so that the desired level of sterilization is achieved. The recycling of the water through the treatment or reaction chamber allows the retention chamber to be smaller than if the water was to be treated in one pass.

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And still another embodiment of the invention is a method and device for treating liquids. The method for treating liquids, preferably water and water like substances, includes providing a sterilizing agent, contacting the living matter in the water with the sterilizing agent, continuing to contact living matter with the sterilizing agent until the desired sterilization level is reached. The water sterilization device has a sterilizing agent source, preferably a sterilizing agent generator which creates a gaseous sterilizing agent for use in a mixing chamber. In the mixing chamber, water is either sprayed or "aerated" into the gaseous sterilizing agent. A return device is connected to the mixing chamber to return the water to its original path.

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In another embodiment of the invention, water treated with the sterilizing agent is recycled to be treated with sterilizing agent repeatedly.

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In another embodiment of the invention, an air sterilization system is connected to a generally closed environment found in aircraft, vessels, vehicles and buildings. The sterilization system intakes air, sterilizes the air using an sterilizing agent and moves the sterilized air into the generally closed environment.

Still another embodiment of the invention is a surface sterilization method and apparatus. The method includes generating a gaseous sterilizing agent, contacting the sterilizing agent with living matter on and around the

surfaces, rendering the living matter non-viable. The apparatus has a sterilizing agent source preferably a sterilizing agent generator described herein, which makes a gaseous sterilizing agent in a sterilization chamber wherein the sterilizing agent contacts living matter making it non-viable.

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Another embodiment of the invention is a liquid-based surface sterilization method and device. The method includes generating ozone, entraining the ozone in water, moving the ozonated water past a UV light, irradiating the water with UV light to form a sterilizing agent, and delivering the sterilizing agent in the water to contact a surface whereby microbes are rendered non-viable. The device for creating and distributing a liquid-based sterilizing agent has a device for supplying O_2 , an ozone generator for converting part of the O_2 to O_3 , a supply of water, a device for diffusing O_3 in the water, a UV source which generates UV, and a device for dispersing the ozonated water after the water was irradiated with UV light creating H_2O_2 and other oxidizing agents.

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In the present invention, "relative humidity" means the ratio of absolute humidity to the maximum possible water vapor in the air at the same temperature. Therefore, the moles of water in vapor in the air would change if relative humidity is held at a constant percentage, but the temperature is changed.

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In the present specification, "ozone" means a gas comprised of significant amounts of O_3 radicals and hydroxyl radicals.

In the present specification, "sterilizing agent" means a substance which renders living matter non-viable. The "sterilizing agent" is a formed by

irradiating ozone in the presence of moisture with ultraviolet light. The "sterilizing agent" has reactive substances, among other things, such as H_2O_2 , ozone, singlet oxygen, hydroxyl radicals, triplet oxygen, and oxygen ions. The "sterilizing agent" can be entrained in a vapor or a liquid

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In the specification, "living matter" means anything having life or anything capable of having life. This definition would include microorganisms, bacteria, germs, viruses, spores, seeds, and plants, such as algae and other cell life, whether individual cells or many cells working together. Typically, living matter is microbial.

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In this invention, "non-viable" means not capable of living, growing, reproducing or developing and functioning successfully.

In this invention, "half-life" means the time it takes for half of a substance to react and change forms. For example, oxygen ions have a shorter half-life than hydrogen peroxide.

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In this invention, "sterilization" does not mean complete destruction of all living matter. Rather, "sterilization" means a reduction in effectiveness of living matter. Some living matter may be destroyed, other living matter may be non-viable. The level of "sterilization" is sometimes specified, for example as a LOG 6 kill. This means that 99.9999% of living matter was rendered non-viable.

Additional objects and advantages of the invention are set forth in the detailed description herein. Also, it should be appreciated that modifications and variations to the specifically illustrated and discussed steps or parts may be practiced in various embodiments and uses of this invention without

departing from the spirit and scope thereof, by virtue of present reference thereto. Such variations may include, but are not limited to, substitution of equivalent steps or parts for those shown or discussed and the reversal of various steps, or the modifications of parts so that generally the same or like results are achieved.

Other objects, features and aspects of the present invention are discussed in greater detail below.

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BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1A is a flow chart of one embodiment of the method of making a sterilizing agent;

Fig. 1B is a flow chart of a second embodiment of the method of making a sterilizing agent;

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- Fig. 2 is a flow chart of an embodiment of the invention for making a sterilizing agent in water;
 - Fig. 3 is a cutaway drawing of the sterilizing agent generation chamber;
- Fig. 4 is a perspective view, partially cut away of an agricultural product storage device;
 - Fig. 5 is an interior view, partially cut away of an agricultural product storage device;
 - Fig. 6A is a sectional view of a device for treating a fluid with a sterilizing agent;
 - Fig. 6B is a sectional view of a fluid mixing device;
 - Fig. 7 is a sectional view of an "aerating" device; and,
 - Fig. 8 is a perspective partially cutaway view of air sterilizing device.

DETAILED DESCRIPTION

It is to be understood by one of ordinary skill in the art that the following description is exemplary of embodiments only and is not intended as limiting the broader aspects of the present invention. The broader aspects are embodied in the exemplary construction.

Referring now to Figs. 1A and B which depict schematics of a sterilizing agent generator 100 for creating a sterilizing agent which can be used to sterilize air, liquids, and surfaces, the generator 100 preferably has an oxygen concentrator 108 or an oxygen source. The oxygen concentrator 108 is operatively connected to an ozone generator 102. The ozone generator 102 is preferably a corona discharge device. A moisture adding device 104 or humidifier is connected in series as shown in Fig. 1A or in parallel as shown in Fig. 1B to the ozone generator 102. The humidifier 104 is connected to sterilizing agent generation chamber 106. In the generation chamber 106, there is a UV lamp 110 that is capable of generating UV light in the range of 220 to 300 nanometers. The wavelength of the UV light is typically between 250 and 260 nanometers and preferably about 254 nanometers. The sterilizing agent generation chamber 106 is connected to a contact or mixing chamber 112 whereby the product to be sterilized, whether air, water, or a surface, is brought into contact with the sterilizing agent so that the sterilizing agent reacts with air, liquid or surface borne microorganisms and other living matter present. The living matter is oxidized or rendered non-viable.

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In operation, the sterilizing agent generator 100 produces a highly effective sterilant called a sterilizing agent that comprises H_2O_2 , oxygen ions, ozone, and hydroxyls. In the first step of the operation of generator 100, oxygen concentrator 108 extracts oxygen from the air. The oxygen concentrator 108 is well known in the art and there are many commercially available oxygen concentrators. At least one oxygen concentrator builds the concentration of oxygen to greater than 50%. Preferably, the oxygen

concentrator produces an oxygen concentration of about 80-100%. The oxygen may be dried so that little or no moisture is left in the oxygen. In air, the natural concentration of oxygen is about 18-21%. Although it is possible to generate a sufficient O_3 concentration from the atmosphere without concentrating the oxygen, a high concentration of oxygen allows for faster, more efficient and greater production of ozone in the ozone generator. In other words, lower concentrations of oxygen can be used to produce results showing effective sterilization; however, exposure time to the sterilizing agent may be significant. The output may be recycled until the desired oxygen concentration is reached. An oxygen sensor may be operably connected to determine the levels of oxygen.

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In certain applications, when trace atmospheric contaminants may be problematic, bottled oxygen may also be used. Bottled oxygen consumes large volumes of oxygen, making the supply of oxygen bottles for large applications a major and costly task. Preferably, the oxygen concentrators are used to minimize the maintenance of the system. The oxygen from the oxygen concentrator is transferred into the ozone generator. In the ozone generator 102, the oxygen is converted from O_2 to O_3 (ozone). As noted above, the ozone is preferably generated through a corona discharge method. The dry oxygen gas provided by the oxygen concentrator 108 is passed between electrodes separated by a gas space and a dielectric. The dielectric is preferably a layer of glass that acts as an insulator. High voltage current is applied to the electrode. A discharge occurs across the gas space and ozone is created by

ionizing a portion of the oxygen that then becomes associated with un-ionized molecules. The reaction is summarized as:

$$O_2 \rightleftharpoons 2O^{-}$$
 $O_2 + O^{-} \rightleftharpoons O_3$

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In actual operation, there are significant quantities of oxygen ions generated. The oxygen ions are very unstable and combine very quickly with other oxygen ions to reform oxygen (O_2) or with oxygen (O_2) to form ozone (O_3) . The oxygen ion is a very good oxidizer which, if utilized fast enough, will provide very good sterilizing results in certain applications discussed below.

The resulting products from the ozone generator are then humidified. In different applications, as discussed below, the concentration of ozone and oxygen ions affects the resulting concentrations of hydrogen peroxide (H₂O₂) and other oxidizing agents. It is also preferred to have a greater concentration of ozone and oxygen ions. In order to reach such greater concentrations, the output of the oxygen concentrator should be at least 97%. Typically, if oxygen of greater than 90% concentration is passed through an ozone generator, ozone comprises .5-8% by weight of the product stream. In certain applications, a high concentration of ozone in the amount of 10% or greater may be desired. This is accomplished by recycling the ozone generator output until the desired concentrations are reached or by any other known means. An ozone sensor may be attached to determine if sufficient ozone is present.

As the concentrations of ozone increase, the resulting product becomes more and more corrosive and explosive. The high concentrations of ozone will corrode the apparatus unless non-corrodible parts are used in the apparatus.

Preferably stainless steel, aluminum, anodized metal, glass, silica, germanium, NOMEX and oxidation resistant coatings, including coatings such as zinc oxide, should be used to limit the corrosive effects of the ozone and subsequent reaction products. In certain applications, high concentrations of reactants are needed and thus expensive corrosion resistant materials should be used. However, in many cases, less corrosive concentrations may be used, thus allowing for less expensive materials to be used in construction of the system.

Another problem that arises with higher concentrations of ozone is the explosivity of the gas. In order to prevent an explosion typically lower concentrations of ozone are used. However, as the ozone concentrations get higher, certain methods to prevent an explosion may be used. For example, by mixing the high concentrations of ozone with an inert gas, explosivity may be reduced. By increasing the reactive components, higher kill ratios of living matter may be achieved.

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After generating ozone in sufficient concentrations for the application, the gas is humidified in humidifier 104. The amount of moisture added by humidifier 104 is dependent on several factors including temperature of the gas chambers, amount of moisture in the gas, gas pressure, and the amount of humidity needed for a particular application.

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Preferably, the air is dry before entering the oxygen concentrator. By drying the air before entering the oxygen concentrator, some undesirable reactions can be avoided. The gases may also be dried after the oxygen concentrator. It is preferred that dry gas with high oxygen concentration is input into the ozone generator. By inputting dry oxygen into the ozone

generator, premature reactions with the ozone forming hydrogen peroxide can be minimized. By decreasing the premature production of hydrogen peroxide and other oxidizing agents, the potency of the resulting sterilant can be increased.

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The ozone enriched gas may be humidified to a desired amount for the application. A humidity sensor may be attached to the ozone enriched gas input so that the humidity of the input into the humidifier can be monitored. The humidity should be generally high. In order to reduce reaction time in the mixing chamber humidity should be above 50%. In some cases, the gas may be saturated, so that the humidity controller will dehumidify the gas to reach the preferred levels.

Regardless, it is desired that humidity of the ozone enriched gas be about 80% to 99% in the hydrogen peroxide generation chamber to maximize the production of OH and $\rm H_2O_2$ molecules. Humidity between 90-94% is preferred for surface and water sterilization systems. For sterilizing air, the humidity is in the range of 40-80%. Preferably the humidity is from 50-70%. The lower humidity allows for a greater production of oxygen ions. In the sterilizing agent generation chamber 106 there is a UV light 110. The UV light emits ultraviolet radiation at levels described above to cause ozone in the presence of moisture to react to form hydrogen peroxide, oxygen ions, and hydroxyls. Preferably, UV light of a wavelength of 253-255 nanometers is used.

In Fig. 2, another sterilant device is shown. It includes an oxygen source. The oxygen leaving the oxygen source 108 is partially converted to ozone in an ozone generating device 102. The ozone/oxygen gas is input into

a water source of reverse osmosis or deionized water 120. The water 120 is irradiated with ultraviolet light 106 to create H_2O_2 and other oxidizing agents. The sterilizing agent impregnated water is rapidly delivered to a contact area 112. The sterilizing agent impregnated water contacts living matter making it non-viable. This method can produce superior results because the reactants created by the UV radiation do not react with anything in the water, thus, more reactant can combine with living material in the contact chamber producing higher kill rates. This method and device can be used in many different ways including washing food stuff, washing surfaces, washing glassware leaving negligible living matter.

Preferably, sterilizing agent is continuously generated but it may be produced in batches. In Figure 8, an air sterilization system is shown. The sterilant may be produced by many methods. In Figure 8, the sterilant is produced in a batch system 802. Ozone is provided to sterilizing agent creation chamber 808 by an ozone source or generator 806. Humidity is added to the sterilizing agent creation chamber 802 by humidity control device 804. Ultraviolet light 810 is inside sterilizing agent creation chamber 802. A mixing device is connected to the sterilizing agent creation chamber 802 to mix and remove the sterilant into contact area 814.

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In operation ozone generator provides 806 a concentration of ozone. Humidity control device 804 adds moisture to the sterilizing agent creation chamber 808. Ultraviolet light 810 irradiates HCOC gas and forms the sterilizing agent. When completed, mixing device moves the sterilizing agent

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into contact area 814 whereby the sterilizing agent makes living matter non-viable.

In a preferred embodiment, the bulb intensity and duration of exposure of UV light is calibrated to the flow of humidity controlled ozone concentrated (HCOC) gas. Preferably, the HCOC gas is pumped through the sterilizing agent generation chamber so that there is short residence time (about 1 to 2 seconds). This residence time can be easily achieved by determining the volume of HCOC atmosphere needed, the intensity of UV light, the concentration of sterilizing agent desired, and the average distance between the HCOC atmosphere and the UV source. Residence time less than 1 second generally produces less sterilizing agent. This may be desirable in certain applications wherein smaller amounts of ozone are desired to be broken down and formed into other oxidizing agents. Although this embodiment is not preferred, it is still within the scope of this invention. If the residence time is greater than 2 seconds, the apparatus and method become less efficient. This is particularly so because after the maximum sterilizing agent concentration is achieved, the reactions to create sterilizing agent are over compensated with the reaction to destroy sterilizing agent with UV being the same energy source for both reactions.

Fig. 3, shows the sterilizing agent creation chamber 300. The sterilizing agent creation chamber 300 includes a germicidal UV light 302. An inlet 304 allows an HCOC gas to enter the chamber to be irradiated with the UV light 302. The UV light emits a germicidal wavelength UV to produce an H_2O_2

atmosphere. An outlet 304 allows for evacuation of the sterilizing agent into a mixing chamber.

Because the reactive elements, hydrogen peroxide, hydroxyl radicals, oxygen ions and ozone, are short lived, it is very difficult to empirically determine the concentrations of each in the resulting sterilizing agent. Therefore, kinetic modeling techniques are used to determine the correct values for the process controls and indirect determination of the relative concentrations of reactants are evaluated based on residual reactivity and rate of kill. The sterilizing agent in the sterilizing agent generation chamber is bled off or pumped out into a reaction chamber 112.

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In the reaction chamber, the reactants hydrogen peroxide, ozone, hydroxyl radicals and oxygen ions contact and react and oxidize living matter. The living matter destroyed or made non-viable can be bacteria including sporulated bacteria, viruses, other single cell and multi-cell organisms, including plants like algae or animals like those causing amoebic dysentery. It is believed that this process can also effectively destroy HIV, anthrax and the Norwalk virus.

It is believed that this basic design and method can be used in many applications. Such applications include air treatment systems, water treatment systems, and surface treatment systems. In any of these systems, the effectiveness of the system may be greatly and easily varied. The systems can produce results comparable or better to the current high volume sterilization systems at a higher rate of sterilization, at a lower operating cost or with less residue or corrosive effects. Alternatively, the sterilizing agent

generator system and method can be tuned to have log 6 and better kills. In the event log 6 or better kills are desired, the method and apparatus are easier to maintain, safer to operate, and more cost effective. Additionally, the sterilizing agent that is unused quickly reacts to form non-harmful substances like oxygen and water, thereby leaving almost no harmful or unpleasant residue.

In one embodiment of the invention, the sterilizing agent generator system and method may be adapted to sterilize the air. The method includes the same steps as described above, including providing oxygen, converting the oxygen into ozone, adjusting the humidity of the ozone to be preferably in a range of 50% and 70%, exposing the humidity adjusted ozone to ultraviolet radiation of about 254 nanometers, forming an sterilizing agent and directing the sterilizing agent into contact with living matter causing the living matter to become non-viable.

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In tests, when exposure times increased, the percent reduction of the viable samples did not significantly change, demonstrating the significant effect of oxygen ions in the sterilizing agent. See Table 1.

Table 1 - Entrained B. subtilis in air

20	Starting Ozone	Relative Humidity	Contact Time	Percent Reduction
	Concentration	·		
	2%	70%	3 min	99.994%
	2%	70%	5 min	99.991%
	2%	70%	15 min	99.997%
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As a result of further testing, it was determined the most effective times for treating living matter in air was between .5 and 5 seconds depending on the concentration of the sterilizing agent. The higher the concentration of the sterilizing agent, the more effective the sterilizing agent is in rendering living matter non-viable. After five seconds, the law of diminishing returns applies. If the living matter continues to be exposed to the sterilizing agent, improved results will be seen. Therefore, the amount of living matter rendered non-viable is a function of time. If absolute sterilization is required, longer sterilization times of up to 45 minutes would ensure that at the appropriate sterilization concentrations. However, if a LOG 3 kill is sufficient, times as short as .5 seconds should suffice. Additionally, sterilization times are related to the type of living matter to be rendered non-viable. To render all HIV viruses in a sample non-viable would take a shorter period of time than to render all Norwalk viruses non-viable. Concentrations of sterilizing agent are limited by the level of resistance to corrosiveness of the system using the sterilizing agent.

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In order to sterilize air effectively, the following principles should be appreciated. Oxygen ions are very reactive but very short lived. Thus, it is desirable to maximize the concentration of oxygen ions in the sterilizing agent when treating air. The primary reason is that the oxygen ions will be quickly and thoroughly mixed to contact virtually all living matter if the living matter is in fluid air. This allows for a short retention time in the mixing or contact chambers.

Another advantage is that the treated gas may be quickly vented if it is passed through a scrubber or catalytic converter. The technology to remove

the remaining ozone, hydrogen peroxide and other oxidizing agents from the treated air are well known in the art. Additionally, filters or other devices to scrub the treated air may be of a less expensive type or require less energy to operate. According to the invention, filters may be used that require a smaller pressure drop. This results in a system being more efficient, including pumps and fans that have less power, consume less electricity and are less expensive to purchase and operate.

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Accordingly, in order to maximize these benefits in air treatment systems the amount of humidity should be carefully controlled. Preferably the humidity level of the HCOC gas is between about 40% and 80%. By limiting the humidity, the levels of H_2O_2 generated by irradiating the HCOC gas with ultraviolet light are reduced and the oxygen ion concentrations are maximized allowing for faster reactions and less retention time.

The maximization of H_2O_2 is beneficial when treating some surfaces. Because the rate of diffusion of sterilizing agent in the air across the surface boundary layer is longer than the life of an effective concentration of oxygen ions and other short lived oxidizing agents, a sterilizing agent with high concentrations of H_2O_2 may be entrained in a liquid and misted over the surface to be treated. In a liquid, the rate of diffusion across the boundary layer allows for effective treatment of the surface with the sterilizing agent. For example, this method may be used to treat meat and packaging material.

In another embodiment of the invention, the sterilization method is adapted to be used to sterilize water. The method includes generating an

sterilizing agent, dispensing the sterilizing agent in the water, contacting the sterilizing agent with living matter to achieve the desired sterilization level.

The generation of the sterilizing agent is accomplished according to the method described herein. In order to achieve better results in treating water, the sterilizing agent can be made with a concentration of ozone preferably between about .75 and 8%. The humidity is preferably about 80-99%. The increased humidity results in the increased concentration of active H_2O_2 molecules which have a longer reaction life than oxygen ions. This longer reaction life is needed so that the longer life reactants, including H_2O_2 , of the sterilizing agent contact the living matter in the water before the reactants reacts to revert back to harmless ingredients H_2O and O_2 .

In tests, substantially higher reduction rates were achieved by increasing the oxidizing agents with longer life spans namely ozone and hydrogen peroxide. See Table 2.

Table 2 – Surface test results with B. subtilis for 15 minutes

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	Starting Ozone	Relative Humidity	Percent
	Concentration		Reduction
	1%	40%	70%
20		70%	91%
		90%	94%
	2%	40%	84%
		70%	98%
		90%	99.4%
25	4%	40%	92%
		70%	99.98%
		90%.	99.92

In a preferred embodiment to treat fluids, as shown in Figs. 6A and 6B, the sterilizing agent is generated by the sterilizing agent generator. The sterilizing agent is then mixed with the water to be treated by diffusing the sterilizing agent into the water with a diffuser 200. The diffuser operates by creating fine bubbles 204 at the bottom of mixing chamber. The fine bubbles rise to the surface contacting living matter and making it nonviable. Alternatively, a Mazzai venturi device which is similar to an injector may be used. Additionally the fluid in the chamber may be mixed with a mixing device 206. Alternatively, the fluid may be mixed in the mixing chamber by moving the treated fluid over baffles 208 and 210 or around other structures in the mixing chamber. Baffles 208, 210 or other similar structures can increase the dwell time/contact time. The increased times allow for higher sterilization and kill rates by allowing more thorough mixing. It also works to have the reactive components revert to their nonreactive ingredients namely water and oxygen.

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In still another embodiment of the invention, an sterilizing agent is created in the mixing chamber whereby water with living organisms is sprayed as a fine mist into the air. In a method similar to aeration, the living organisms contact the sterilizing agent so that the living organisms are made non-viable.

The mechanism for "aerating" water shown in Fig. 7, in an H_2O_2 atmosphere is well known in the art. A mixing chamber 220 contains the sterilizing agent. Needle nozzles 222, spray the fluid or water into the air in a very fine mist. The sterilizing agent contacts the living organisms rendering them non-viable.

In yet another embodiment of the invention, the sterilizing agent is entrained in a solution such as water whereby the solution is finely sprayed on a surface. This method is ideal for treating meats, agricultural products such as fruit and vegetables, and other surfaces. This method works also very well on conveyor systems. The object is sprayed, rotated and sprayed again. This can be accomplished while the object to be treated is moving down an assembly line. This method is far superior to the current method disclosed in Castberg '759 wherein a UV light activates an ozone atmosphere in contact with the surface containing the microorganism. In the '759 patent there are significant problems with shadowing. Shadowing is the effect the container has on the path of the UV light so that some parts of the container are shielded or shadowed from the UV radiation thus making sterilization of the entire surface virtually impossible. By having a reactive atmosphere contact the entire surface, the shortcomings of the '759 patent among others are avoided.

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An agricultural storage device 400 shown in Fig. 4 is an enclosed structure having a roof 402 and exterior walls 404. The roof 402 has at least one air vent 406 that allows the interior atmosphere to communicate with the exterior atmosphere. The agricultural storage device 400 has at least one opening 408 so that vehicles 410 or machines 412 may deliver or remove agricultural products. An air handling device 414 communicates with the atmospheres inside and outside the agricultural storage device 400. A control system 416 controls the air handling device 414. The air handling device 414 is operably connected to a sterilization device 418 which is described herein. The control system 416 may also control the sterilization device 418.

The interior of the agricultural storage device as shown in Fig. 5 has agricultural products 500 stored on grates 502 or in other open areas so that air may circulate around and through the piles of agricultural products. The sterilization device periodically releases a sterilizing agent 504 which is moved around and through the piles of agricultural products 500 either continuously or intermittently, producing biostatic or biocidal environment. The selection of a biocidal or biostatic environment is based on operational considerations of the storage facility and are not limited by the technology. Circulating devices 506 are controlled by control system (not shown) to maximize the sterilant effect. A venting system may be needed to evacuate any residual sterilant before an operator enters.

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In yet another embodiment of the invention, a method of storing goods, preferably agricultural products or food stuffs, includes the steps of generating a sterilizing agent, and periodically circulating the sterilizing agent around the food stuffs so that biological growth is inhibited. By periodic circulation of the reactant atmosphere, biological organisms will be prevented from destroying the food stuffs. In a preferred embodiment, the food stuffs are washed with a sterilant before being stored in a warehouse or container whereby periodic exposure to a reactive atmosphere inhibits additional living matter growth.

In another embodiment of the invention a control system determines if the environment in the containment area, mixing chamber, or contact chamber is at safe levels for entry thereto.

In yet another embodiment of the invention, a medical waste sterilization device has a input device for inputting medical waste, a shredder or grinder

mechanism for making the medical waste into a desired size or physical condition, treating the medical waste with a remotely generated sterilizing agent as described herein, and retaining the medical waste in the medical waste sterilization device until the desired level of sterilization is achieved.

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It should be further understood by those of ordinary skill in the art that the foregoing presently preferred embodiments are exemplary only and that the attendant description thereof is likewise by way of words of example rather than words of limitation, and their use does not preclude inclusion of such modifications, variations and/or additions to the present invention as would be readily apparent to one of ordinary skill in the art, the scope of the present invention being set forth in the appended claims.

Claims:

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- 1. A method of making living matter non-viable comprising the steps of: providing a highly concentrated oxygen source of at least 95% O₂; converting part of the oxygen into ozone so that an ozone atmosphere has a concentration of ozone between .5% and 8% by weight of the mixture; regulating the moisture content of the ozone atmosphere to have humidity greater than 70%; irradiating the moisturized ozone atmosphere with ultraviolet radiation having a wavelength in a range of 230 and 270 nanometers; creating a sterilizing agent remotely comprising H₂O₂, O₂, OH, and oxygen ions; transporting the sterilizing agent to a contact area; and, applying the sterilizing agent to living matter rendering the living matter non-viable.
- 2. A method of making living matter non-viable according to claim 1, further comprising the step of promoting a reaction with the sterilizing agent so that the sterilizing agent reverts to primarily water and oxygen.
- 3. A method of creating a gas for sterilizing water comprising the steps of: providing an oxygen gas having a concentration of oxygen of at least 95% by weight; converting at least part of the oxygen to ozone; controlling the humidity of the oxygen and ozone gas so that the relative humidity of the gas is from 80%-99%; irradiating the humidity controlled gas with ultraviolet radiation of a wavelength of 253 to 255 nanometers; continuing to irradiate the gas for 1 to 2 seconds to form a sterilizing agent; and, applying the sterilizing agent to living matter rendering the living matter non-viable.

4. A method of sterilizing gas comprising the steps of: creating a gaseous sterilizing agent having at least H_2O_2 , O_2 , O_3 , and oxygen ions and water vapor; moving the gaseous sterilizing agent to a contact chamber; and, mixing the sterilizing gas with air in the contact chamber so that at least 95% of all living matter in the air is rendered non-viable in 5 seconds or less.

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- 5. A method of creating a sterilizing agent from oxygen, water and electricity comprising: creating an initial gas having in the range of .5% to 10% ozone from oxygen and electricity; regulating the humidity of the gas by adding water so that the humidity of the gas is in the range of 40% to 100% of saturation; using electricity to generate ultraviolet light in the range of 200 nanometers to 300 nanometers; and, directing the ultraviolet light at the initial gas so that oxidizing agents are produced which include H_2O_2 .
- 6. A method of sterilization comprising: generating an sterilizing agent in concentrations of at least 1% by weight to sterilize; exposing living matter to said sterilizing agent; and, keeping said living contaminants exposed to the sterilizing agent for no more than 45 minutes so that at least 99.999% of living matter is destroyed.
- 7. A method of sterilization according to claim 6, wherein the step for generating sterilizing agent comprises: providing O_3 of a concentration in the range of .5 to 8% by weight for the generation of sterilizing agent; providing

moisture so that the relative humidity of O_3 is above 40%; and, providing UV radiation in the range of 250 to 260 nanometers in the presence of the O_3 and the moisture to generate at least 1% sterilizing agent by weight.

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- 8. A method of sterilization comprising: generating O₃ from oxygen so that the O₃ comprises from .75% to 10% of the atmosphere by weight; providing a relative humidity of at least 50%; exposing the O₃ in the presence of humidity to UV radiation to form a concentration of hydrogen peroxide of at least .5% by weight in the reactive mixture for sterilization of living matter whereby living matter is exposed to the concentration of hydrogen peroxide and other oxidizing agents so that 99% of the living matter is rendered non-viable in less than 15 minutes.
- 9. A method of sterilization according to claim 8, wherein the sterilizing agent is in contact with the living matter for no greater than 5 minutes.
- 10. A method of sterilization according to claim 8, wherein the sterilizing agent is in contact with the living matter for no greater than 2 minutes.
- 11. A method of sterilization according to claim 8, wherein after twenty minutes the sterilizing agent has fully reacted and no reactive residue is left on any surface exposed to sterilizing agent.

12. A method of sterilization according to claim 8, wherein the relative humidity is between in the range of 80% and 95%.

- 13. A method of sterilization according to claim 8, wherein the relative humidity is 90% to 92%.
- 14. A method of sterilizing agricultural products with a sterilizing agent comprising: generating a sterilizing agent having a concentration of reactive components in the range of 1% to 10% by weight; and, washing or immersing the agricultural products or food stuffs in the sterilizing agent so that at least 99% of living matter on the surface of the agricultural products or food stuffs is made non-viable.

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- 15. A method of sterilizing agricultural products with a sterilizing agent according to claim 14, comprising the further step of periodically rewashing the agricultural products or food stuffs so that the agricultural products are not destroyed by living matter.
- 16. A method of sterilizing potatoes with a sterilizing agent comprising the steps of: washing the potatoes in an atmosphere having a concentration of 1% to 10% sterilizing agent by weight; storing the potatoes in a container; and, circulating a sterilizing agent in a concentration in a range of 1% to 10% by weight so that growth of living matter is inhibited.

17. A method of sterilizing fluids containing living matter comprising: creating an atmosphere having a concentration of sterilizing agent of 1% to 10% by weight; and, mixing the atmosphere with the fluid so that at least 95% of all living matter is made non-viable.

- 18. A method of sterilizing liquids containing living matter comprising the steps of: creating an atmosphere having a concentration of 1%-15% sterilizing agent; and bubbling the atmosphere through the liquids so that at least 95% of all living matter is made non-viable.
- 19. A method of sterilizing liquids containing living matter comprising the steps of: creating an atmosphere having a concentration of 1%-15% by weight sterilizing agent; and, aerating the liquid through the atmosphere so that at least 95% of all living matter is destroyed.
- 20. A method of sterilizing waste water or runoff water containing living matter, comprising the steps of: separating at least part of the water from a water source; treating the water with a gas having a concentration in the range of 1% to 10% sterilizing agent; and, returning treated separated water to remainder water.

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21. A method of sterilizing of waste water or runoff water according to claim 20, comprising the additional step of recycling the treated water for at least one additional treatment with the sterilizing agent.

22. A sterilizing agent generating device comprising: an ozone source; a UV source; and a moisture source whereby the O_3 source provides O_3 in a concentration sufficient so that when O_3 in the presence of moisture is exposed to UV radiation of a given frequency, strength and duration, a sterilizing agent is produced that has a concentration of 1% to 15% by weight.

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- 23. A sterilizing agent generating device according to claim 22, wherein the concentration of sterilizing agent may be tuned to individual applications by varying at least one of UV intensity, UV duration, starting ozone concentration and humidity.
- 24. A sterilizing agent generating device according to claim 22, further comprising at least one sensing device to signal the presence of at least one of O_3 , H_2O_2 , UV and moisture.
- 25. A sterilization device comprising: an ozone source; a UV source; a moisture source; a mixing device; and a dwell device whereby a sterilizing agent is created by generating UV from the UV source in the presence of O₃ and moisture generated from the O₃ and moisture sources, then the sterilizing agent is mixed by the mixing device to apply the sterilizing agent to the living matter and the sterilizing agent continues to contact living matter in a dwell device making living matter non-viable until a preselected sterilization level is reached.

26. A method of sterilizing potable water, comprising the steps of: generating a gas having 1% to 10% sterilizing agent by weight; and, mixing the gas with the potable water for a period of time so that at least 95% of all living matter is made non-viable.

FIG. IA

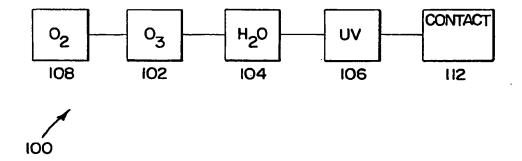


FIG. IB

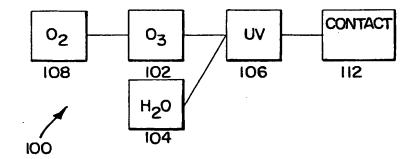
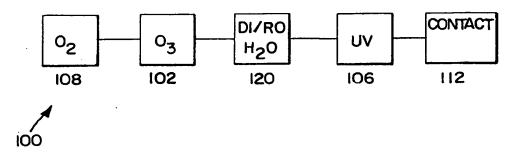
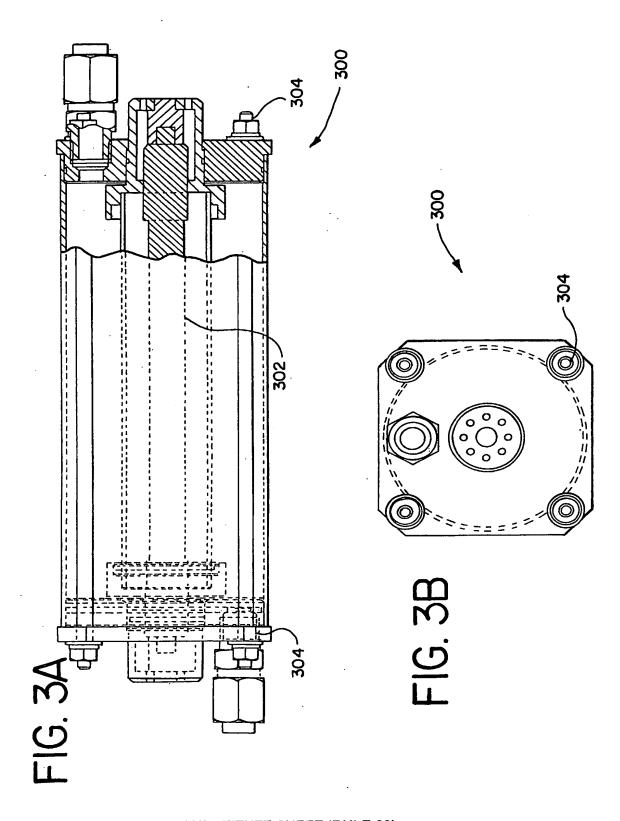


FIG. 2





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FIG. 4

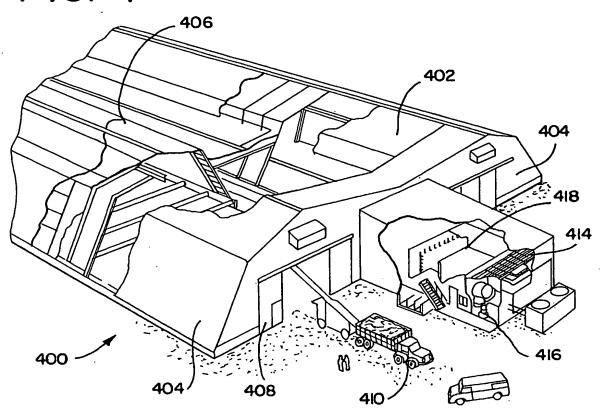


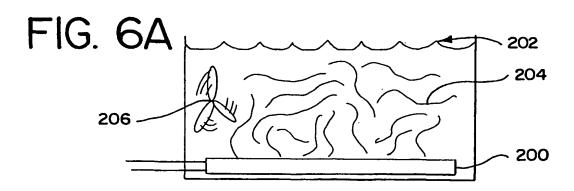
FIG. 5

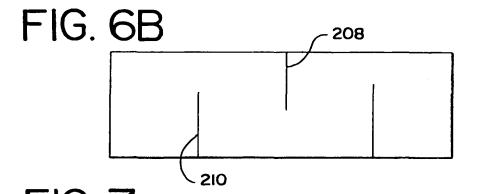
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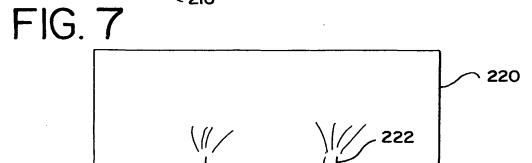
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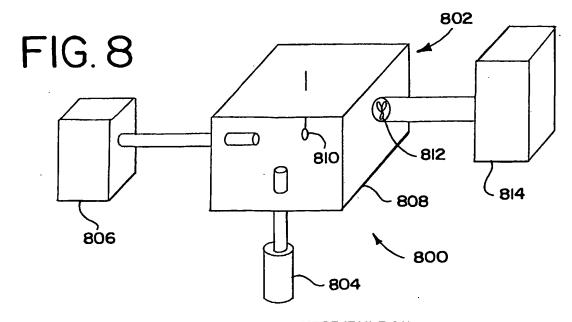
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INTERNATIONAL SEARCH REPORT

International application No.

PCT/US01/11553

A. CLASSIFICATION OF SUBJECT MATTER IPC(7) : A61L 2/10, 2/18; C02F 1/78; A23B 7/157, 7/158 US CL : 422/23, 24, 28, 29, 30, 32, 292; 210/759, 760; 426/320								
	According to International Patent Classification (IPC) or to both national classification and IPC							
B. FIEL	DS SEARCHED							
	Minimum documentation searched (classification system followed by classification symbols) U.S.: 422/23, 24, 28, 29, 30, 32, 292; 210/759, 760; 426/320							
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched NONE								
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) Derwent: ozone, UV, hydroxyl								
	UMENTS CONSIDERED TO BE RELEVANT							
Category *	Citation of document, with indication, where a		Relevant to claim No.					
X	JP 60-153982 A (TOSHIBA KK) 13 August 1985 (·						
Y	US 4,959,142 A (DEMPO) 25 September 1990 (25		21					
X	US 5,213,759 A (CASTBERG et al) 25 May 1993		6					
Y	US 5,227,184 A (HURST) 13 July 1993 (13.07.93		16, 18					
X	US 5,656,242 A (MORROW et al) 12 August 1997	7 (12.08.97), see entire document.	1-5, 8-13					
Y			7					
x	US 5,816,498 A (SMITH, JR. et al) 06 October 19	998 (06.10.98), see entire document.	14, 15					
Y			16					
X . M	US 5,824,243 A (CONTRERAS) 20 October 1998	(20.10.98), see entire document.	17, 19, 20, 26					
Υ Υ			18, 21					
x	US 5,858,435 A (GALLO) 12 January 1999 (12.0)	1.99), see entire document.	14, 15					
X	JP 11-9948 A (TAKAHASHI) 19 January 1999 (19	9.01.99), see English abstract.	22-24					
X	JP 2000-70971 A (TAGUCHI et al) 07 March 2000	0 (07.03.00), see English abstract.	22-24					
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Date of the actual completion of the international search 27 June 2001 (27 06 2001) Date of mailing of the international search report 26 JUL 2001			rch report					
27 June 2001 (27.06.2001) Name and mailing address of the ISA/US Authorized officer								
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